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by

RALPH P. SEWARD

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A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE GRADUATE DEPARTMENT OF BROWN UNIVERSITY, 1925

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I. Introduction

The mutual solubility relations of salts in aqueous solution are markedly regular and have been the subject of extensive investigation. Apparently, a corresponding study of salt solubilities in non-aqueous solvents has not been made. This problem was originally attacked by Dr. A. B. Stowe[1] who worked chiefly with acetone. The difficulties inherent in the problem were not completely overcome but his results showed clearly that, in general, the solubility relations parallel those in water, that is, on adding a salt with a common ion, the solubility is depressed while, on adding a salt without a common ion, the solubility is increased.[2]

The present investigation was undertaken for the purpose of obtaining accurate data with respect to the solubility relations of salts in one or more non-aqueous solvents. Much time was spent in an attempt to obtain results with acetone, but the instability of the solvent rendered the problem extremely difficult so that only a limited series of satisfactory measurements was finally obtained. Isopropyl alcohol was then chosen, since it is stable and may be readily purified. The order of magnitude of the solubility of ordinary salts in this solvent is also exceptionally favorable.

The ultimate aim of this investigation was to gain an insight into the phenomena peculiar to solutions of electrolytes. In order to disentangle the complex phenomena of electrolytic solutions, it is necessary to simplify the problem by working at rather low concentrations. Hitherto, the conductance method has been used almost exclusively in the study of solutions in non-aqueous solvents at low concentrations. Unfortunately, the results of conductance measurements can not be safely interpreted at the present time. The freezing or boiling point method has not thus far been satisfactorily developed in the case of non-aqueous solvents, even at concentrations as high as 0.01 N. It seemed, therefore, that the solubility method might afford the readiest means of investigating the behavior of non-aqueous salt solutions at concentrations as low as 10^{-3} N or lower.

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[1] Allen B. Stowe: Dissertation, Clark University (1923).

[2] Recently King and Partington [Transactions of the Faraday Society, **23**, 522 (1927)], have determined the solubility of sodium iodide in ethyl alcohol in the presence of lithium iodide and sodium thiocyanate. Their results are in agreement with our observations in that the solubility of the saturating salt is diminished on the addition of a salt with a common ion. A detailed comparison of their results with ours is not possible because of the great difference in the solubility of the saturating salts.

The mutual solubility effects of salts in aqueous solutions have recently been critically reviewed by A. A. Noyes.[1] He concludes that they are in substantial agreement with the interionic attraction theory of Debye and Hückel.[2] The results of the present investigation make it possible to test the same theory in the case of solutions in non-aqueous solvents having a value of the dielectric constant in the neighborhood of 20.

II. Materials

Acetone. Commercial acetone was purified by the bisulphite method. Final dehydration was accomplished by treating the solvent with finely powdered boric oxide. This method of dehydration proved very satisfactory but the solvent itself was found to be relatively unstable so that the solubility of the salt changed as the age of the solvent increased.

Isopropyl Alcohol. Commercial petrohol, 91% isopropyl alcohol, was treated with powdered sodium hydroxide. The alcohol layer was distilled and the same process of dehydration repeated until a satisfactory product was obtained. The purified product has a density of 0.785 at 25° and a specific conductance of about 1.5×10^{-7}.

Salts. The best grade of salts were twice recrystallized from water. Sodium chloride was purified by dissolving in hot water and precipitating with hydrogen chloride. All salts were dried before using.

III. Method and Procedure

The method of determining the solubility of the salt consisted in agitating a quantity of the solvent containing a known amount of the added salt and an excess of saturating salt until saturation was reached and then analyzing the solution for the saturating salt. About 5 g. of the saturating salt were finely pulverized in an agate mortar and introduced into a special bottle of cylindrical form, having a length of approximately 38 cm., a diameter of 10 cm., and a capacity of 3 liters. A known weight of the second salt, also finely ground, was introduced into the same bottle and then a known weight of pure solvent (about 2 liters) was introduced from the stock container.

The bottles were provided with narrow necks of about 12 mm. internal diameter with well ground stoppers which were held in position, water tight, by means of special rubber caps. Four bottles were affixed to a spindle which was rotated in a horizontal position under water maintained at a temperature of 25 ±.01°. Initially, the bottles were rotated for 12 hours at a temperature of 28°-30° after which the temperature was lowered to 25° and rotated for 6 hours longer. The bottles were then removed from the spindle and set upright without removing from the thermostat and allowed to settle for 3 hours or more. Two samples of 500 cc. or more were then blown from the bottle into glass stoppered Erlenmeyer flasks, the exact amount of solution being

[1] Arthur A. Noyes: J. Am. Chem. Soc., **46**, 1098 (1924).

[2] Debye and Hückel: Physik Z., **24**, 185; Debye: 334 (1923); Rec. Trav. chim., **42**, 597 (1923).

determined by weight. The solvent was then evaporated, the residue containing the salts was transferred to a beaker and the content of the saturating salt determined analytically.

By far the most convenient salts were combinations of alkali metal halides with nitrates, the halide serving as saturating salt. In this case the halide was determined by precipitation with silver in the usual manner. The concentration of the second salt was known from the amount initially added. In one or two instances, in which the second salt was present up to the saturation point, the amount was determined analytically. At the low concentration of the solutions used, the density did not differ appreciably from that of the pure solvent, hence no correction was made for this factor.

IV. Solubility Effects in Acetone

Only a single series of satisfactory measurements was obtained in the case of this solvent using sodium bromide as saturating salt and sodium nitrate as added salt. The results are given in Table I, concentrations being expressed in millimols per liter.

TABLE I

Solubility of Sodium Bromide in Acetone at 25°
in the presence of Sodium Nitrate

$NaNO_3$	NaBr(Anal.)	NaBr(Mean)	$(\Sigma c_i)^{\frac{1}{2}} \times 10^3$	$-\frac{1}{2} \log P_{io}/P_i$
0.00	0.7674	0.7677	39.07	0.0000
	.7680			
0.1371	0.7594	0.7597	40.68	.0315
	.7601			
0.2286	0.7436	0.7462	41.48	.0457
	.7488			
0.6602	0.7152	0.7129	45.68	.1102
	.7105			

V. Solubility Effects in Isopropyl Alcohol

In this solvent, the solubility of sodium chloride was determined in the presence of sodium nitrate and ammonium nitrate. The solubility of sodium chloride was particularly favorable, being less than 0.5×10^{-3}. With a combination of sodium chloride and sodium nitrate, the analytical procedure worked out very well. In the case of sodium chloride and ammonium nitrate, however, the procedure was less satisfactory as is evidenced by the lack of satisfactory agreement between check determinations. The difficulty was probably due, in part at least, to the volatility of ammonium salts, some loss perhaps occurring in the removal of the alcohol.

The results of the solubility determinations of sodium chloride in the presence of sodium nitrate and ammonium nitrate are given in Tables II and III respectively. In view of the analytical difficulties mentioned in connection with mixtures of sodium chloride and ammonium nitrate, the highest values, rather than the mean, are employed in the subsequent dis-

cussion. These results are somewhat more concordant than are the mean values although the difference would not materially alter the nature of the results. Concentrations are expressed in millimols per liter.

TABLE II

Solubility of Sodium Chloride in Isopropyl Alcohol at 25°
in the presence of Sodium Nitrate

$NaNO_3$	NaCl(Anal.)	NaCl(Mean)	$(\Sigma_{Ci})^{\frac{1}{2}} \times 10^3$	$-\frac{1}{2}\log P_{io}/P_i$
0.0000	0.4242	0.4246	29.14	0.0000
	.4251			
0.0800	0.4147	0.4159	31.50	.0292
	.4172			
0.1672	0.4057	0.4050	33.84	.0544
	.4044			
0.4013	0.3812	0.3817	39.57	.1098
	.3822			
0.5902	0.3657	0.3625	43.64	.1412
	.3594			
0.5984	0.3650	0.3640	43.87	.1442
	.3631			
0.8539	0.3502	0.3480	49.16	.1827
	.3459			
1.3097	0.3245	0.3242	57.16	.2340
	.3239			
1.5574	0.3196	0.3244	61.32	.2645
	.3293			
1.9590	0.3081	0.3074	67.31	.2936
	.3087			
2.8240	0.2899	0.2903	78.91	.3501
	.2908			

TABLE III

Solubility of Sodium Chloride in Isopropyl Alcohol at 25°
in the presence of Ammonium Nitrate

NH_4NO	NaCl(Anal.)	NaCl(selected)	$(\Sigma_{Ci})^{\frac{1}{2}} \times 10^2$	$-\frac{1}{2}\log P_{io}/P_i$
0.0000	0.4565	0.455	30.16	0.0000
	.4541			
0.0985	0.4741	0.481	34.12	.0241
	.4811			
0.1839	0.4838	0.503	37.06	.0436
	.5034			
0.3537	0.5346	0.547	42.45	.0800
	.5466			
0.6938	0.6175	0.617	51.20	.1323
	.6096			
1.4024	0.7342	0.734	65.35	.2027
	.6850			

VI. Influence of Water on the Solubility of Sodium Chloride in Isopropyl Alcohol

In the course of this investigation it was soon found that the solubility of various salts was measurably influenced by the presence of traces of water. In order to eliminate any uncertainty due to the presence of water, the influence of water on the solubility of pure sodium chloride, as well as on that of mixtures of sodium chloride and sodium nitrate was investigated.

In Table IV are given values of the solubility of sodium chloride in isopropyl alcohol in the presence of varying amounts of water. The density of the solvent mixture was determined and the concentrations are expressed in millimols of salt per liter of the mixture.

TABLE IV

Solubility of Sodium Chloride in Isopropyl Alcohol at 25° in the presence of Varying Amounts of Water

% H_2O	NaCl(Anal.)	Density	% H_2O	NaCl(Anal.)	Density
0.000	0.4246	0.7849	1.39	0.8025	.7885
0.084	0.4399	.7854	2.02	1.100	.7900
0.815	0.6034	.7868	5.88	4.138	.7985

To a large quantity of solvent, 2.02% of water was added and the solubility of sodium chloride determined in the presence of varying amounts of sodium nitrate. The results are given in Table V, concentrations being expressed in millimols per liter.

TABLE V

Solubility of Sodium Chloride in Isopropyl Alcohol at 25° containing 2.02% of Water in the presence of Sodium Nitrate

$NaNO_3$	NaCl(Anal.)	NaCl(Mean)	$(\Sigma c_i)^{\frac{1}{2}} \times 10^2$	$-\frac{1}{2}\log P_{i_0}/P_i$
0.0000	1.1004	1.0999	46.90	0.0000
	1.0994			
0.1707	1.0780	1.0796	50.00	.0238
	1.0813			
0.2697	1.0672	1.0679	51.71	.0360
	1.0687			
0.4370	1.0460	1.0560	54.64	.0576
	1.0660			
0.8842	1.0112	1.0139	61.60	.1007
	1.0167			
1.3597	0.9694	0.9723	68.30	.1364
	.9752			
2.4412	0.9107	0.9123	81.90	.2014
	.9140			
6.534	0.7985	0.7984	121.1	.3424
	.7984			

VII. Discussion

Concordance of Results. Considering the analytical difficulties, chiefly due to the low solubility of the salts studied, the concordance of the data obtained is fairly satisfactory. This is particularly true of the solubility of sodium chloride in anhydrous and hydrated isopropyl alcohol in the presence of sodium nitrate. With few exceptions, the analytical values agree within less than 1% and the points lie on smooth curves. In Fig. 1 (upper curve) is shown the solubility of sodium chloride in isopropyl alcohol in the presence

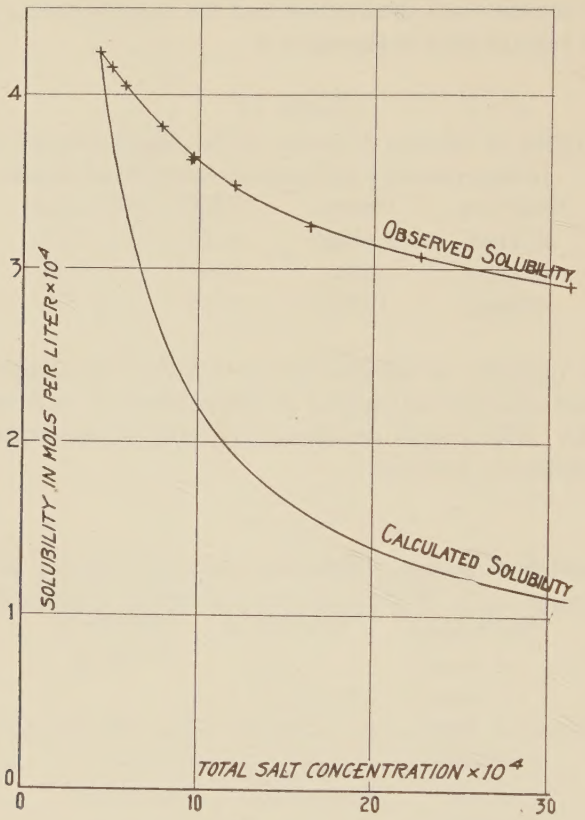

FIG. 1

Comparison of Solubility of Sodium Chloride in Isopropyl Alcohol in the presence of Sodium Nitrate with Value calculated according to Interionic Attraction Theory.

of sodium nitrate as a function of the total salt concentration. As may be seen from the figure, only the 9th point is seriously in error. The two analytical determinations in the case of this point are not in agreement, one of the values being much too high, as is evident from the fact that the solubility as found is greater than at the preceding lower concentration of sodium nitrate. If the high value is rejected, the point conforms well with the curve as drawn. The determinations with sodium chloride in hydrated alcohol, as well as with sodium bromide in acetone, are in good agreement. The

determinations of the solubility of sodium chloride in the presence of ammonium nitrate show considerable variation, probably for the reason already mentioned. However, it is believed that the higher values chosen are not seriously in error.

Comparison with Aqueous Solutions. Roughly, the influence of a uni-univalent salt on the solubility of another salt of the uni-univalent type is much the same in isopropyl alcohol and acetone as it is in water. It is noteworthy that the depression due to an added salt with a common ion is much smaller in isopropyl alcohol and acetone than in water, while the increase in solubility, due to the addition of a salt without a common ion, is much greater in isopropyl alcohol than in water.

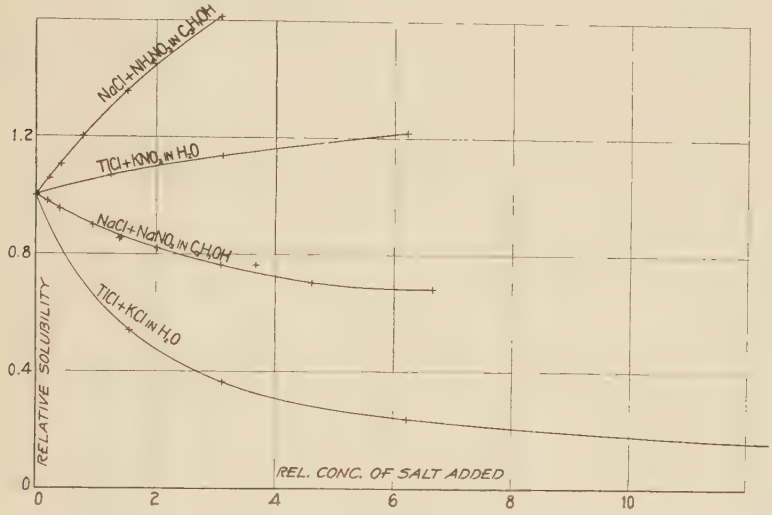

FIG. 2
Relative Solubility Effects in Water and Isopropyl Alcohol compared.

In order to compare the solubility effects, in the present case, with similar effects as observed in aqueous solutions, it is necessary to reduce the concentrations to a common unit. This is conveniently done by dividing the observed values of the solubility, as well as the concentration of the added salt, by the solubility of the saturating salt in the pure solvent. The relative concentrations so obtained thus represent the concentration of a given constituent in terms of the concentration of the saturating salt in the pure solvent. For the purpose of comparison, the relative solubilities and relative concentrations of added salt have been calculated for solutions of thallous chloride in water in the presence of potassium chloride and of potassium nitrate[1] and for sodium chloride in isopropyl alcohol in the presence of sodium nitrate and of ammonium nitrate. The relation between relative solubilities and relative concentrations of added salt is shown graphically in Fig. 2. Some of the values as read from the smooth curves at round relative concentrations are given in Table VI.

[1] Bray and Winninghof: J. Am. Chem. Soc., 33, 1670 (1911).

TABLE VI

Comparison of Solubility Effects in Isopropyl Alcohol and Water

	Relative Concentrations				
C added Salt	0.2	0.5	1.0	2.0	3.0
S (TlCl in H_2O + KCl)	0.90	0.78	0.65	0.47	0.41
S (NaCl in C_3H_7OH + $NaNO_3$)	0.98	0.94	0.90	0.82	0.77
S (TlCl in H_2O + KNO_3)	1.01	1.03	1.06	1.10	1.13
S (NaCl in C_3H_7OH + NH_4NO_3)	1.05	1.13	1.25	1.44	1.60

As may be seen from Fig. 2, or from Table VI, the solubility of thallous chloride in water, on the addition of potassium chloride, is depressed much more than is that of sodium chloride in isopropyl alcohol on addition of sodium nitrate. For example, on the addition of a second salt, corresponding to 0.2 of the concentration of the saturating salt in the pure solvent, the solubility of thallous chloride is depressed 10% while in isopropyl alcohol the solubility of sodium chloride is depressed only 2%. On the addition of a salt of concentration equal to that of the original salt in pure water, the solubility in the case of thallous chloride is depressed 35% while in isopropyl alcohol the solubility of sodium chloride is depressed only 10%. This means that on adding 16.07 millimols of potassium chloride ($S_o = 16.07 \times 10^{-3}$) to a solution of thallous chloride in water, the solubility is depressed 35% while on the addition of 0.4246 millimols of sodium nitrate ($S_o = 0.42 \times 10^{-3}$) to sodium chloride in isopropyl alcohol, the solubility is depressed only 10%. Roughly, therefore, the depressing effect, of a uni-univalent salt on the solubility of a second uni-univalent salt with a common ion is about three and a half times as great in water as it is in isopropyl alcohol. To obtain the same relative depression in isopropyl alcohol as in water, the relative concentration of added salt must be six times as great as in water.

The increased solubility of a uni-univalent salt on addition of a uni-univalent salt without a common ion is much greater in isopropyl alcohol than it is in water. This may be seen from the upper curves of Fig. 2 as well as from Table VI. For example, at a concentration of the added salt corresponding to the relative value 0.2, the solubility of thallous chloride in the presence of potassium nitrate is increased 1%, while that of sodium chloride in the presence of ammonium nitrate in isopropyl alcohol is increased approximately 5%. For a relative concentration of 1.0, the increase of solubility is 6% and 25% respectively in water and isopropyl alcohol. In round numbers, the increase of solubility of a uni-univalent salt in isopropyl alcohol on addition of a second salt without a common ion is about four times as great as it is for a corresponding pair of salts in water. Expressed in other terms, to obtain the same relative increase of solubility in water as in isopropyl alcohol, the relative concentration of added salt in water must be six times that in the alcohol.

The Influence of Water. The effect of water on the solubility of salts in non-aqueous solvents is of considerable significance since, in the interpretation of solubility data, it is necessary to know to what extent water may have

a disturbing influence. The addition of water to isopropyl alcohol results in a marked increase in the solubility of sodium chloride. This is evident from Table V or Fig. 3. Thus, the addition of 2% of water, or 0.886 mols per liter, raises the solubility from 0.4246×10^{-3} to 1.10×10^{-3} mols per liter. The lower curve in Fig. 3 shows that the solubility increases more rapidly than the concentration of the added water. The logarithm of the solubility

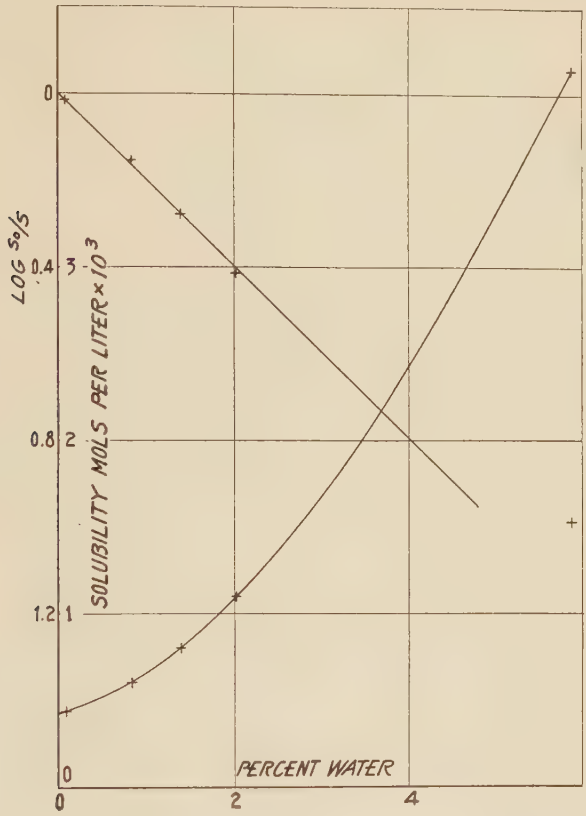

Fig. 3
Showing how the Solubility of Sodium Chloride in Isopropyl Alcohol is influenced by addition of Water.

increases approximately as a linear function of the concentration of water except for the most concentrated solution, as may be seen from the upper curve of Fig. 3. We might interpret this by saying that the thermodynamic potential of the salt in solution is diminished on the addition of water and, if the thermodynamic potential varies as the logarithm of the concentration, then the thermodynamic potential of the salt varies approximately as a linear function of the water concentration. Such an interpretation, however, has no physical significance for only unhydrated salt, either as ions or ion pairs, can be in immediate equilibrium with the pure solid phase. What fraction of the salt is present in the unsolvated condition, we have no means of knowing, but it is probably very small. On the other hand, we have good reason for

believing that the addition of water leads to a disturbance of the solvate equilibrium with the formation of hydrated ions and ion pairs. The formation of new molecular species, on addition of water, raises the solubility. Since we have no knowledge of the fraction of salt present in an unsolvated condition, the interpretation of the thermodynamic potentials, or activities, in terms of stoichiometric concentrations leads to purely fictitious results in the physical sense.

If we assume hydration of the salt to occur according to the equation:

$$(a) \quad MX + nH_2O = MX(H_2O)_n$$

and if the law of mass action is applicable, we obtain for the solubility of the salt the expression:

$$(1) \quad S = S_o + \frac{S_o C^n_{H2O}}{K}$$

where S is the solubility of the salt in the presence of water, S_o is its solubility in the pure solvent, C_{H_2O} is the concentration of water (mols per liter), K is the equilibrium constant of reaction (a), and n is the number of molecules of water associated with one molecule of salt. C_{H_2O} may be assumed equal to the total concentration of water since only a small fraction of it is associated with the salt. For sodium chloride in the presence of water in isopropyl alcohol, we obtain the values K = 0.47 and n = 1.58. The concentrations as calculated by means of equation (1), using these constants, do not deviate greatly from the observed values with the exception of the point at the lowest concentration which may well be in error owing to the small solubility change and the possible presence of traces of water. The value n = 1.58 may be considered as the mean hydration of the salt. The actual phenomena involved are doubtless more complex than has been assumed and we can place no great weight on the result. Nevertheless it is of interest to note that the value obtained for the hydration of the salt is reasonable as to order of magnitude.

While the addition of 2% of water to isopropyl alcohol increases the solubility of sodium chloride to approximately two and one-half times its value in the pure solvent, the relative solubility effect, on addition of sodium nitrate, differs but little from that in the pure solvent. In Fig. 2, the curve, passing through points indicated by crosses, represents the relative solubility of sodium chloride in pure isopropyl alcohol in the presence of sodium nitrate. If the corresponding curve is calculated for the hydrated alcohol, it is found to rise only a little above that for the pure solvent. It must be concluded, therefore, that, although the order of magnitude of the solubility effects is much increased on addition of water, the relative solubility effects remain substantially unchanged.

The Interionic Attraction Theory. It is of interest to compare the solubility effects observed with the requirements of the interionic attraction theory of Debye and Hückel. As already mentioned, A. A. Noyes has made

a careful study of the solubility effects in water from this point of view and has concluded that the results are in substantial agreement with this theory. A corresponding examination of the results presented in this investigation indicates that these are not in agreement with the interionic attraction theory. For purposes of comparison, Noyes' method has been adopted. As Noyes has shown, according to the theory, the following equation should hold for uni-univalent salts:

$$(2) \quad -\tfrac{1}{2}\log\frac{P_{io}}{P_i} = \beta[(\Sigma C_i)^{\frac{1}{2}} + (2C_o)^{\frac{1}{2}}].$$

In this equation P_{io} is the product of the ion concentrations of the saturating salt in the pure solvent and P_i the same product for the salt in the mixture, assuming complete ionization. β is a constant involving the temperature and the dielectric constant of the solvent, ΣC_i is the total concentration of ions, positive and negative, in the solution and is therefore equal to twice the total salt concentration and C_o is the concentration of the saturating salt in the pure solvent. Obviously, for two salts with a common ion, $P_{io} = C_o^2$ and $P_i = C_a(C_a + C_b)$, where C_a is the concentration of the saturating salt in the mixture and C_b the concentration of the added salt. In the case of two salts without a common ion $P_i = C_a^2$. In water, the constant β has the value 0.357 at 25°. Assuming the dielectric constants[1] of acetone and isopropyl alcohol to be 22 and 20 respectively, we find for β in these solvents the values:

$$\beta \text{ (acetone)} = 2.24, \ \beta \text{ (alcohol)} = 2.79.$$

In Fig. 4 are plotted values of $-\frac{1}{2}\log P_{io}/P_i$ against those of $(\Sigma C_i)^{\frac{1}{2}}$. According to the interionic attraction theory, this plot should be linear and the slope should correspond to the value of β for the solvent in question. In Fig. 4 the straight lines, as drawn, correspond to the theoretical curves for isopropyl alcohol and acetone. It will be seen from the figure that the experimental points lie far below the theoretical straight lines and that, moreover, the plots are distinctly curved even up to the lowest concentration of added salt. The divergence of the curve for sodium chloride in the presence of sodium nitrate is markedly greater than that for the same salt in the presence of ammonium nitrate. The divergence in the case of sodium bromide in the presence of sodium nitrate in acetone is markedly greater than in that of sodium chloride in isopropyl alcohol. How great the divergence is between observation and theory, is illustrated in Fig. 1, in which are plotted the actual and calculated values of the solubility of sodium chloride in isopropyl alcohol in the presence of sodium nitrate. Solubilities are plotted as ordinates and and total salt concentrations as abscissas. The upper curve represents the observed values; the lower curve calculated values according to equation (2)l

[1] A satisfactory value for the dielectric constant of isopropyl alcohol does not appear in the literature. The value adopted is probably not greatly in error, as appears on comparison with the value of this constant for related alcohols.

assuming for the dielectric constant of isopropyl alcohol the value 20. In the case of salts without a common ion, the divergence is equally striking.

The divergence of the experimental results from those required according to the interionic attraction theory bears no apparent relation to the dielectric constant. In order to bring the observed values in the more dilute solutions into conformity with the theory it would be necessary to assume for the dielectric constant the value 5.3 for acetone with sodium bromide and sodium

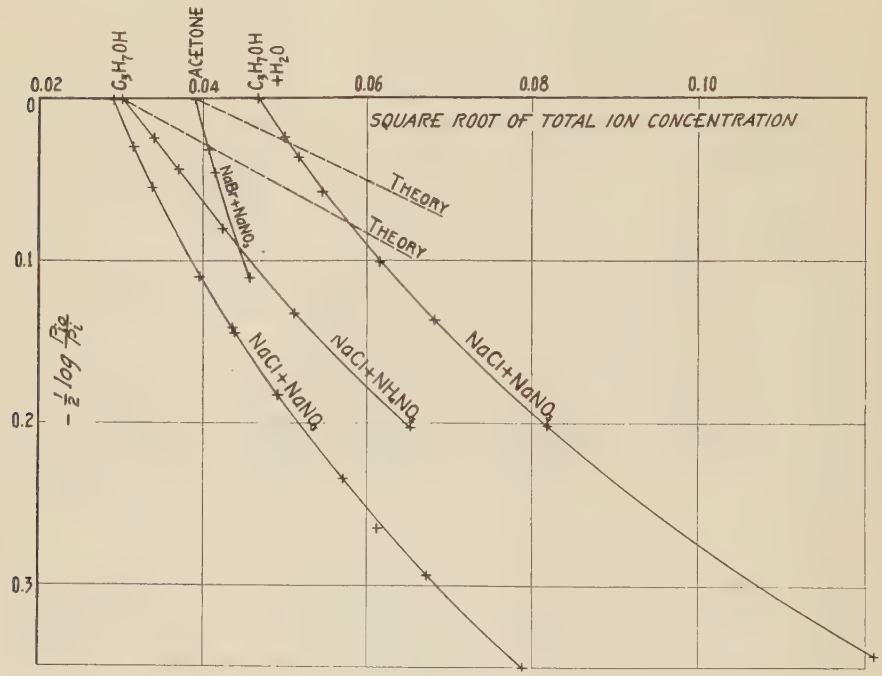

Fig. 4

Comparison of Solubility Effects in Acetone and Isopropyl Alcohol with the Interionic Attraction Theory.

nitrate; 7.2 for isopropyl alcohol with sodium chloride and sodium nitrate, and 11.4 with sodium chloride and ammonium nitrate, and 9.7 for the hydrated alcohol with sodium chloride and sodium nitrate.

The values thus calculated for the dielectric constant would appear to preclude the possibility of accounting for the present discrepancies on the basis of a change in the dielectric constant due to the added salts. In all these cases the total salt concentration is of the order of 10^{-3} or less. Evidently, the dielectric constant is not the determining factor in these solutions. Thus, the dielectric constant of acetone, if anything, is greater than that of isopropyl alcohol, yet the deviation for acetone is much greater than for isopropyl alcohol. In the latter solvent, the deviations are much greater for the combination sodium chloride-sodium nitrate than for sodium bromide-ammonium nitrate, while for the hydrated alcohol, the deviations are

markedly smaller than for the pure solvent. While the addition of 2% of water would doubtless increase the dielectric constant slightly, there is no reason for believing that this would be sufficient to account for the observed results.

It seems evident that the mutual solubility effects of salts are characteristic not only of the salt but also of the solvent and it is reasonable to look for an explanation of the phenomena in a specific interaction between the solvent molecules and the ions or ion pairs of the salt.

The discrepancies between the values observed and those predicted according to the interionic attraction theory are so great that it is difficult to see how they can be reconciled without introducing new concepts. While the theory has met with marked success in the case of aqueous solutions it seems doubtful that it will meet with equal success in the case of solutions in non-aqueous solvents. If the solubility effects as observed in water may be looked upon as a confirmation of the theory, then the corresponding effects observed in the case of non-aqueous solutions must weigh equally against it.

It would seem that in electrolytic solutions in solvents of lower dielectric constant it will be necessary to assume that the process of ionization is incomplete. Solutions of salts in non-aqueous solvents, generally, behave much as do aqueous solutions of weak acids and bases. The ultimate solution of the problem is, perhaps, to be looked for in a combination of the interionic attraction theory with some other concept that takes into account the mechanism of the ionization process. The theory takes account of the mutual forces acting between the ions, once they exist as such, but it tells us nothing with regard to the process by which these ions come into existence.

With decreasing value of the dielectric constant the force acting between a pair of ions increases, and it is not unreasonable to suppose that ion pairs may approach each other sufficiently closely to act as a unit from the kinetic point of view. The process of ionization would then consist in supplying to such an ion pair a sufficient amount of energy to separate the ions against the attractive force of their charges. This would naturally depend upon the nearness of approach of the ions and the spatial configuration of their electronic systems, as well as the dielectric constant of the solvent medium. There are not a few facts that are in agreement with this point of view. In a given solvent, ionization depends mainly on the effective ion diameters which in some cases may correspond to ion diameters as determined for pure salts and in others as determined for solvated ions in solution. The formation of solvated ions involves specific factors relating to both the ions and to the solvent molecules. According to this view, the affinity of the negative ion for an electron has nothing to do with the tendency of the salt to ionize; for this does not affect the energy required to separate a pair of ions. The affinity of a positive ion for an electron may, however, be directly involved.

It should be pointed out that, qualitatively, the results of the present investigation are in agreement with the view that electrolytes are incompletely ionized in solvents having dielectric constants of intermediate value. The low depression of the solubility of a salt on the addition of another salt with

a common ion and the great increase of solubility on the addition of a salt without a common ion lend support to the view that unionized molecules, that is, ion pairs, exist in these solutions. It may be foreseen that in the case of solvents having still lower dielectric constants than those here investigated, the mutual solubility effects may become relatively very large for salt pairs without a common ion, even at low concentrations of the added salt.

Summary

The influence of uni-univalent salts on the solubility of other uni-univalent salts in acetone and in isopropyl alcohol has been investigated. These include sodium bromide in the presence of sodium nitrate in acetone, sodium chloride in the presence of sodium nitrate and ammonium nitrate in isopropyl alcohol and sodium chloride in the presence of sodium nitrate in hydrated isopropyl alcohol.

The solubility effects in these solvents resemble those in water, that is, the solubility of a given salt is depressed on addition of a second salt with a common ion and is increased on addition of a second salt without a common ion. The solubility depression in these solvents is about one-fourth that in water while the increase, on addition of a salt without a common ion, is about four times as great as in water.

The results obtained have been examined from the standpoint of the interionic attraction theory of Debye and Hückel. The observed effects are much smaller than predicted according to the theory.

It is suggested that, in order to account for the observed effects, the interionic attraction theory will have to be supplemented by other assumptions which take into account the specific interactions between the ions and the solvent as well as between the ions themselves.